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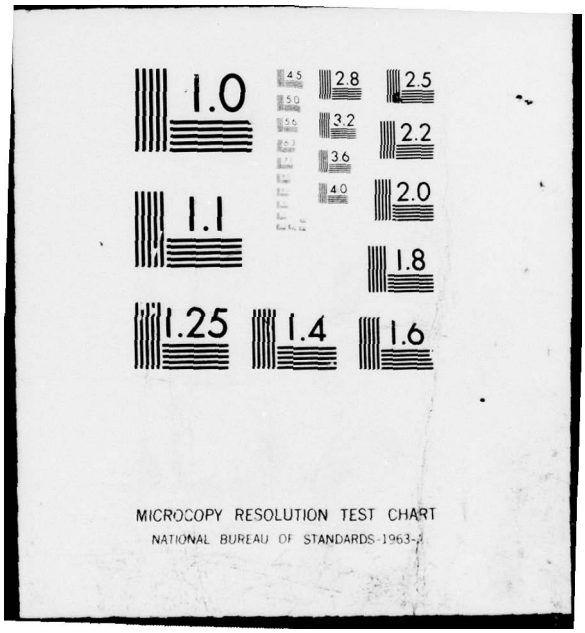
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TETRADECAISOPROPOXYDIHYDRIDOTETRATUNGSTEN, (IV). OXIDATIVE ADDITION OF PrO-H ACROSS A TUNGSTEN-TO-TUNGSTEN TRIPLE BOND.

by

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The title compound $W_4(OPr^i)_{14}(H)_2$ is formed in the reaction between $W_2(NMe_2)_6$ and Pr^iOH and has been characterized by a single crystal X-ray study. Formation of this novel tetranuclear complex is accounted for by the following sequence of reactions: (i) alcoholysis, $W_2(NMe_2)_6 + 6Pr^iOH \rightarrow W_2(OPr^i)_6 + 6HNMe_2$, (ii) oxidative addition of Pr^iO-H across a W≡W, $W_2(OPr^i)_6 + Pr^iO$-H $\rightarrow W_2(OPr^i)_7(\mu$-H) W=W distance = 2.446(1) Å and (iii) association by Pr^iO bridge formation. $2W_2(OPr^i)_7(\mu$-H) $\rightarrow W_4(OPr^i)_{14}(H)_2$.

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Tetradecaisopropoxydihydridotetratungsten (IV). Oxidative Addition of PrO-H across a Tungsten-to-Tungsten Triple Bond.

Sir:

Bimetallic compounds containing metal-to-metal multiple bonds[1] will occupy an important position in the development of transition metal cluster chemistry.[2] They are the smallest examples of unsaturated cluster compounds and should provide building blocks for the synthesis of new polynuclear cluster compounds. Furthermore their reactions should complement those well documented in mononuclear transition metal chemistry.[3] We wish now to report the preparation and characterization of a novel tetranuclear tungsten compound which illustrates these considerations.

Hydrocarbon solutions of $W_2(NMe_2)_6(W\equiv W)$[4] react rapidly with isopropanol at room temperature with the liberation of amine. Upon removing the solvent a black solid of empirical formula $W(OPr^i)_3$ based on elemental analysis[5] was obtained. The black substance gave very complex nmr spectra and was thermally unstable yielding propylene, isopropanol and traces of water as volatiles when heated above 80°C in vacuum. These observations contrast with the reaction between $Mo_2(NMe_2)_6$ and isopropanol which yields the thermally stable and well characterized compound $Mo_2(OPr^i)_6(Mo\equiv Mo)$.[6] Additional study of the reaction between $W_2(NMe_2)_6$ and isopropanol in a sealed system showed that along with dimethylamine a gas non-condensable in liquid N_2 was formed. The latter was identified as molecular hydrogen by mass spectroscopy. The solids obtained from the reaction between

$W_2(NMe_2)_6$ and isopropanol are extremely soluble in hexane and give upon careful crystallization the title compound $W_4(H_2)(OPr^i)_{14}$ in about 50% yield based on tungsten.

The presence of hydrogen atoms in bridging positions was deduced in the following way:

(1) An x-ray crystallographic study[7] initially showed the structure in Fig. 1, with the bond distances and angles in Table I. The molecule resides on a crystallographic inversion center (between W(1) and W(1)'). The outer tungsten atoms, W(2) and W(2)', are coordinated to three terminal and two bridging OPr^i ligands while the inner tungsten atoms, W(1) and W(1)', are coordinated to one terminal and four bridging OPr^i ligands. Each tungsten atom is thus coordinated to five oxygen atoms and the WO_5 polyhedra are distorted square pyramids.

(2) According to these results the compound would have to be either a mixed valence compound, $W_4(OPr^i)_{14}$, or an alcoholate, $W_4(OPr^i)_{12}(Pr^iOH)_2$. The mixed valence formulation would have difficulty accounting for the diamagnetism (as shown by nmr) and is more directly discredited by the observation that reaction of $W_2(NMe_2)_6$ with isopropanol containing Pr^iOT gave a product containing tritium.[8]

(3) However, the presence of Pr^iOH was rendered very doubtful by the absence of any i.r. or nmr evidence for a hydroxyl group and by the fact that the compound does not react with pyridine to form $W_2(OPr^i)_6(py)_2$, even though the latter compound has been shown to exist and has been fully characterized[9] as a species containing a triple-bond (W≡W = 2.332(1)Å).

(4) These results required us to search for some other formulation and we were reminded of the $[Mo_2X_8H]^{3-}$ ions[10] which have recently been shown directly by x-ray crystallography[11] to contain μ-H atoms. The apparent absence of one bridging ligand between the two tungsten atoms in each half of the tetratungsten structure was highly reminiscent of the apparent[10a,b] absence of a third bridging ligand in the $[Mo_2X_8H]^{3-}$ species, later shown to be present as a hydrogen atom.[10c,11] To test the correctness of the formula $W_4(OPr^i)_{14}(\mu\text{-}H)_2$, the following two experiments were done.

(5) The ^1H nmr spectrum at 220 MHz in toluene-d_8 and benzene-d_6 at 25° was found to contain in addition to the expected Pr^iO resonances (1.34 ppm (doublet) and 5.27 ppm (septet), each with $J_{HH} \approx 6.3$ Hz) a singlet at 7.96 ppm (all positions downfield from TMS). The singlet had satellites due to coupling to ^{183}W (I = 1/2; 14.4% of natural abundance) with $J_{WH} = 95$ Hz. Since a cryoscopic molecular weight measurement had shown that the tetranuclear structure is largely or totally maintained in solution, we are forced to attribute the simplicity of the spectrum to some process that scrambles the OPr^i groups. Since only one pair of satellites is observed on the 7.96 ppm signal this same process (or some other one) must make the tungsten atoms equivalent so that we see only one ^{183}W-^1H coupling constant. It should be remembered that we see only those molecules that contain one ^{183}W.

(6) We now returned to the x-ray data, encouraged by the fact that in the $[Mo_2X_8H]^{3-}$ ions[11] and in numerous other species with M(μ-H)M units the μ-H atoms have been detected and refined. We have found that there is evidence for a μ-H atom between W(1) and W(2) and that it can be refined successfully as such, to give W(1)-H = 1.61(8)Å, W(2)-H = 1.89(8)Å, W-H-W = 88(4)° deg. with the isotropic temperature factor for μ-H equal to $1 \pm 2 Å^2$.

We therefore conclude that each tungsten atom is 6-coordinate as shown in Fig. 2. All qualitative features of the structure are now understandable. The W-O bonds trans to μ-H are considerably longer than those trans to μ-OPr^i, which exactly parallels the situation in the $[Mo_2Cl_8H]^{3-}$ ion.[11] The μ-H is closer to W(1) so as to minimize the imbalance in electron density distribution that the difference in formal oxidation numbers in a symmetrical structure (W(1) = + 3 1/2 and W(2) = + 4 1/2) would tend to create.

Formation of the title compound in the reaction between $W_2(NMe_2)_6$ and Pr^iOH may be attributed to the following reaction steps: (i) alcoholysis, $W\text{-}NMe_2 + Pr^iOH \rightarrow W\text{-}OPr^i + HNMe_2$. (ii) Oxidative addition, $W_2(OPr^i)_6 + Pr^iOH \rightarrow W_2(OPr^i)_7(\mu\text{-}H)$. (iii) association by Pr^iO bridge formation. The W(1)-W(1)' distance implies no metal-metal bonding, whereas the W(1)-W(2) distance, 2.446(1)Å, is quite consistent with the presence of a W=W bond.[12] Our studies on these and related compounds are continuing.[13]

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2. Potential catalytic implications of cluster chemistry have recently been discussed. See E. L. Muetterties, Bull. Soc. Chim. Belg. 1975, 84, 959; E. L. Muetterties, Science, 1977, 196, 839; R. Ugo, Catal. Rev., 1975, 11, 225.

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4. M. H. Chisholm, F. A. Cotton, M. W. Extine and B. R. Stults, J. Am. Chem. Soc., 1976, 98, 4477.

5. Analysis: Calcd: C, 29.93; H, 5.86; found: C, 30.2; H, 5.96.

6. M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, Inorg. Chem., 1977, 16, 1801.

7. Cell constants: $a = 12.645(4)\text{Å}$, $b = 13.157(4)\text{Å}$, $c = 9.788(3)\text{Å}$, $\alpha = 102.43(2)°$, $\beta = 67.80(2)°$, $\gamma = 101.05(2)°$ and $V = 1461.5(7)\text{Å}^3$. The structure was solved in the centrosymmetric space group $P\bar{1}$. A total of 3782 unique data having $0° < 2\theta_{MoK\alpha} < 45.0°$ was measured, of which those 2949 having $I > 3\sigma(I)$ were used in subsequent refinement. All atoms were refined to convergence utilizing anisotropic thermal parameters for the tungsten and oxygen atoms and isotropic thermal parameters for the carbon atoms. The final cycle of least squares refinement, including the μ-H atoms, gave $R_1 = 0.037$ and $R_2 = 0.052$.

8. We thank Professor Charles Gilvarg of the Department of Biochemistry Princeton University for his assistance and guidance in these experiments.

9. This compound is obtained by reaction of $W_2(NMe_2)_6$ with Pr^iOH in pyridine, Cf. M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. Little and P. E. Fanwick, Inorg. Chem., submitted for publication. The structure is analogous to that found for $Mo_2(OSiMe_3)_6(HNMe_2)_2$ by M. H. Chisholm, F. A. Cotton, M. W. Extine and W. W. Reichert, J. Am. Chem. Soc., 1978, 100, 153.

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12. A W=W bond with a length of 2.530(2)Å has recently been reported by A. Bino, F. A. Cotton, Z. Dori and J. C. Sekutowski, Inorg. Chem., 1978, 17, 2946. Re=Re bonds have long been known in $Re_3X_9L_3$ type compounds and have bond lengths of ca. 2.47Å; Cf. M. J. Bennett, F. A. Cotton and B. M. Foxman, Inorg. Chem., 1968, 7, 1563 and earlier papers cited therein.

13. We thank the Office of Naval Research and the National Science Foundation for support at Indiana and Princeton Universities and the Robert A. Welch Foundation for support at the Texas A&M University. M.H.C. was an Alfred P. Sloan Foundation Fellow, 1976-1978.

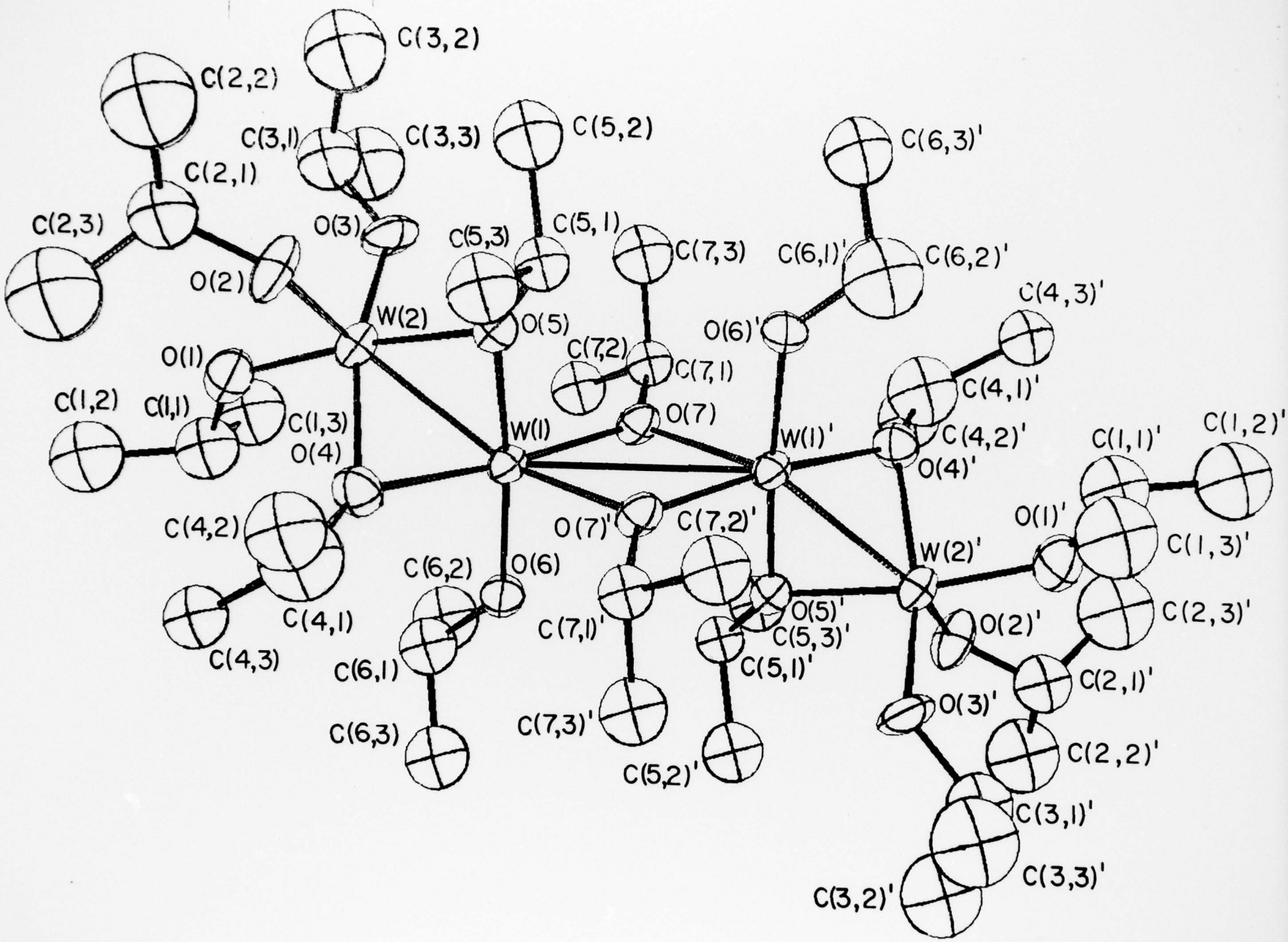
Table 1

Some Bond Lengths and Angles in $W_4(OPr^i)_{14}$*

Distances, Å		Angles, Deg.	
W(1)-W(1)'	3.407(1)	O(4)-W(1)-O(5)	78.2(3)
W(2)	2.446(1)	O(6)	91.7(3)
W(1)-O(4)	2.101(7)	O(7)	173.4(3)
O(5)	2.005(7)	O(7)'	107.6(3)
O(6)	2.897(6)	O(5)-W(1)-O(7)	95.2(3)
O(7)	2.038(6)	O(7)'	86.6(3)
O(7)'	2.187(6)	O(6)	168.6(3)
W(2)-O(1)	1.904(8)	W(1)-O(4)-W(2)	70.9(2)
O(2)	1.959(7)	O(5)-W(2)	73.1(2)
O(3)	1.892(7)	O(1)-W(2)-O(2)	91.9(3)
O(4)	2.116(6)	O(3)	94.3(3)
O(5)	2.100(7)	O(2)-W(2)-O(3)	101.7(3)
		O(1)-W(2)-O(4)	94.5(3)
		O(5)	169.9(3)
		O(2)-W(2)-O(4)	90.5(3)
		O(5)	85.2(3)
		O(3)-W(2)-O(4)	164.6(3)
		O(5)	95.8(3)

*We give here the final values after refinement with the μ-H atoms included. These differ by only about <0.004A or <0.01° from those obtained without the μ-H atoms.

Fig. 1. A view of the entire $W_4(OPr^i)_{14}$ molecule, omitting the μ-H atoms.


C(3,2)
C(2,2)
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C(3,3)
C(5,2)
C(6,3)'
C(2,1)
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O(3)
C(5,3)
C(5,1)
C(7,3)
C(6,1)'
C(6,2)'
O(2)
W(2)
O(5)
C(4,3)'
O(6)'
O(1)
C(7,2)
C(7,1)
C(4,1)'
C(1,2)
C(1,1)
C(1,3)
O(7)
C(4,2)'
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C(1,2)'
W(1)
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C(2,1)'
O(3)'
C(7,3)'
C(6,3)
C(2,2)'
C(5,2)'
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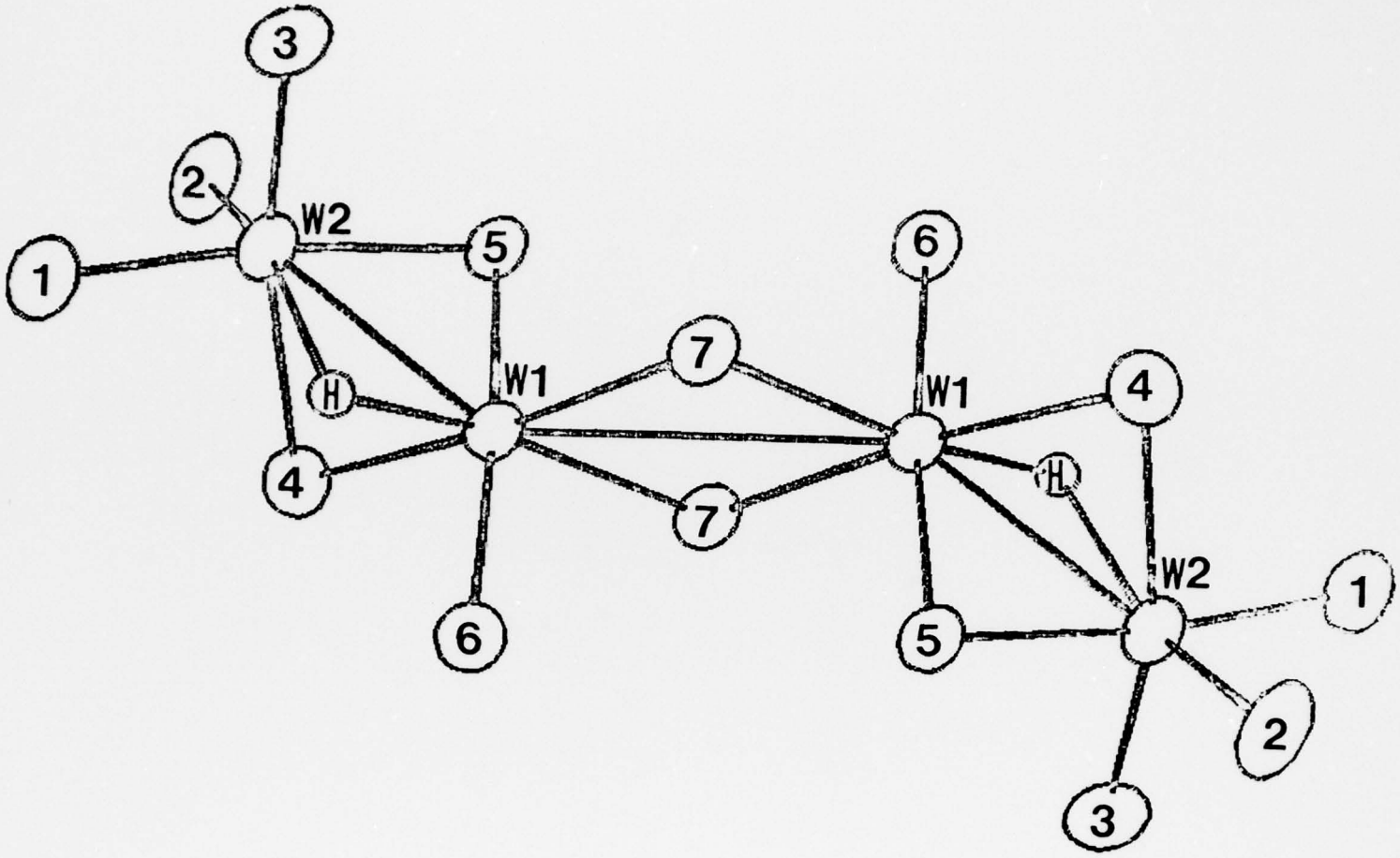
C(3,2)'

Fig. 2. A view of one confacial bioctahedron, W_2O_8H, moiety, showing the bridging hydrogen atom.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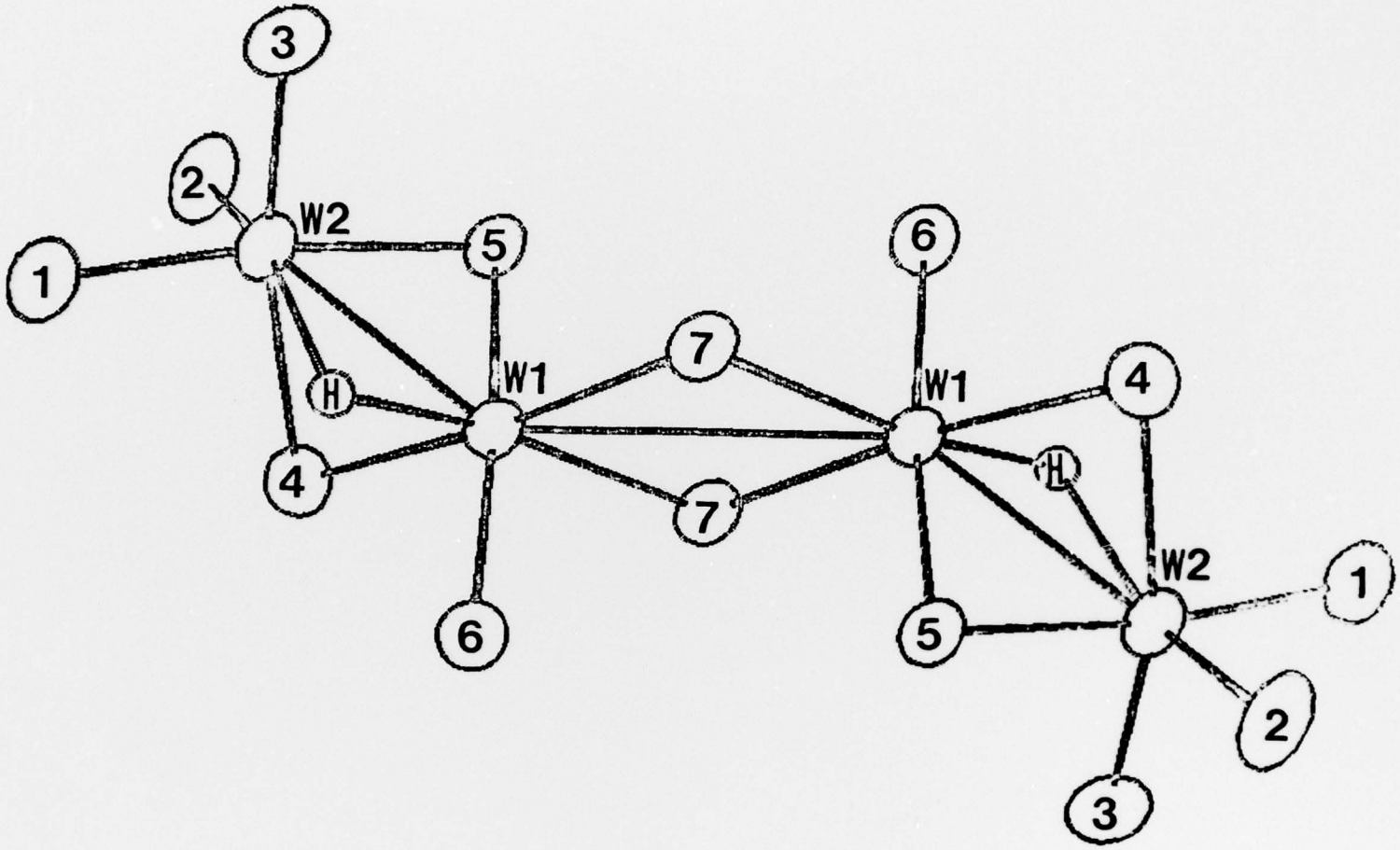
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